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# Chromium Complexes Supported by Bidentate Thioether-Imine [N,S] Ligands: Synthesis and Ethylene Oligomerization Studies

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A series of new Cr(III) complexes of general formula [Cr{N,S}(THF)Cl<sub>3</sub>] (**2a**, N,S = PhS-2-PhCH=N-<sup>1</sup>Bu; **2b**, N,S = PhS-2-PhCH=N-C<sub>6</sub>H<sub>4</sub>-4-OMe; **2c**, N,S = PhS-2-PhCH=N-C<sub>6</sub>H<sub>5</sub>; **2d**, N,S = <sup>1</sup>BuS-2-PhCH=N-C<sub>6</sub>H<sub>5</sub>) were prepared and characterized by elemental analysis, IR spectroscopy and ESI-HRMS. DFT calculations confirm that *mer* isomers are more stable by 23.9-34.3 kcal mol<sup>-1</sup> than the *fac* isomers. Upon activation with methylaluminoxane (MAO), chromium precatalysts **2a-2d** showed moderate activity in ethylene oligomerization (TOF =  $3.4-26.6 \times 10^3$  (mol ethylene)(mol Cr)<sup>-1</sup>·h<sup>-1</sup> at 80 °C) with Schultz-Flory distribution of oligomers ( $K_{C4-C12} \approx 0.90$ ) and production of polymer varying from 1.2 to 9.8 wt.%. The amount of 1-butene is the largest component in the liquid fraction suggesting that these precatalysts operate via a Cossee-Arlman mechanism. The catalytic activity is mainly controlled by electronic effects at the thioether/imine groups. In general, the precatalysts bearing electron-donating substituents (*tert*-butyl, p-C<sub>6</sub>H<sub>4</sub>OMe) (**2a**, **2b** and **2d**) showed higher activities in comparison to **2c** containing an electron-withdrawing (i.e., phenyl) substituent. Notably, the MAO loading has strong influence on the activity of **2a**. Thus, the use of 2000 equiv. led to a remarkable increase in the catalytic activity [TOF = 971,100 (mol ethylene) (mol Cr)<sup>-1</sup> h<sup>-1</sup>] with high selectivity to formation of oligomers (98.8 wt.%).

# 1. Introduction

Linear  $\alpha$ -olefins (LAO) are important petrochemicals precursors for preparing linear low-density polyethylene (LLDPE), plasticizers, surfactants for detergents, base stock, additives for synthetic lubricants, and alcohols for plasticizers.<sup>1</sup> Several commercial processes (Shell, Ineos, IFP/Sabic Alphabutol®, Sabic/Linde Alpha-SABLIN® and Chevron-Phillips) produce a wide distribution of LAO carbon chain lengths from  $C_4$  to  $C_{20}$ .<sup>2</sup> Furthermore, several companies (e.g. CPChem and Sasol) have successfully commercialized a tri/tetramerization technology for the production of 1-hexene and 1-octene.<sup>3</sup> The last decades have witnessed the development of several class of chromium complexes containing a large variety of bidentate and tridentate ligands.<sup>4</sup> While, the vast majority of these ligands comprise primarily of phosphorus and/or nitrogen as donor atoms, just a few examples of S-based ligands have been used in the synthesis of active chromium species.<sup>5</sup> McGuinness, Wasserscheid and co-workers reported a highly efficient new series of chromium catalysts for the trimerization of ethylene based bis-(2-alkylsulphanyl-ethyl)-amine (SNS) ligands. For instance, the activation of [bis-(2-ethylsulphanyl-ethyl)amine]CrCl<sub>3</sub> (A, Chart 1) with 280 equiv. of MAO yield an extremely high active catalytic system (TOF = 298 900 h<sup>-1</sup>; 160

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**Chart 1**. Examples of chromium complexes for oligomerization catalysis based on S-based ligands.

In 2005, the same research group reported a detailed study of this system evaluating the effect of central donor atom and chelate ring size.<sup>5c</sup> For instance, the replacement of NH central donor group by phenylphosphino (PPh) unit [(EtSCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>PPh (SPS)] did not lead to selective trimerization, but rather a Schulz-Flory distribution of olefins along with production of higher amount of polymer. Complex CrCl<sub>3</sub>[(EtSCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)N(H)(CH<sub>2</sub>CH<sub>2</sub>SEt)] (**B**, Chart 1) which contains an expansion of the chelate ring on one side of the

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<sup>+</sup> Electronic Supplementary Information (ESI) available: Tables S1-S6 and Figures S1-S10. See DOI: 10.1039/x0xx00000x

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ligand rise to an active trimerization catalyst. However, the activity of this complex is less than half that of its symmetrical analogue A, and selectivity toward C<sub>6</sub> is likewise lower.

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Gambarotta, Duchateau and co-workers have shown that activation of Cr(III) complex bearing 2,6-bis(RSCH<sub>2</sub>)pyridine [R= Ph, Cy] with MAO in toluene led to a highly selective catalysts for the production of  $1-C_{6}$ .<sup>5d</sup> For instance, [(2,6-(CySCH<sub>2</sub>)2-py)CrCl<sub>3</sub>] (**C**, Chart 1) when treated with 500 equiv. of MAO exhibited moderate activity (5177 g/gCr·h<sup>-1</sup>) producing almost exclusively 1-hexene (99.6 mol %).

More recently, Makume and co-workers described a systematic process condition optimization study using P,Sbidentate ligand/Cr(acac)<sub>3</sub> catalyst system.<sup>5d</sup> Depending on the reactions conditions the amount of solids was dramatically reduced, while maintaining reasonable activities and very high liquid product selectivity. Under optimized conditions (2 equiv. of ligand, 960 equiv. MMAO, 50 °C, 100 mL MCH, 45 bar 2-(cyclohexylthio)phenyl](2ethylene, 30 min.), the isopropylphenyl)(phenyl)phosphine/Cr(acac)<sub>3</sub> catalyst system (D, Chart 1) showed high catalytic activity (575 691 g/gCr/h) together with relatively low solids (5.2%), 61.2% 1-octene selectivity and 75.6% 1-octene + 1-hexene combined in the liquid oligomer fraction.

As part of our continuing interest in developing catalytic oligomerization systems, the present contribution focuses on the synthesis of Cr(III) complexes bearing bidentate thioether-Imine [N,S] (**E**, chart 1) aiming to evaluate the catalytic potential of them in ethylene oligomerization. Under optimized oligomerization conditions this class of Cr catalysts display high activities with a Schulz–Flory olefin distribution. This paper will discuss the oligomerization results, evaluating the role of the ligand, and the experimental parameters on the activity, selectivity, and product distribution.

# 2. Results and discussion

# **2.1.** Synthesis and characterization of chromium complexes bearing thioether-imine bidentate ligands

The thioether-imine ligands (**1a-1d**) were synthesized by Schiff base condensations between the primary amines and the corresponding thioether benzaldehyde in methanol. Treatment of **1a-1d** with  $CrCl_3(THF)_3$  in THF yielded after workup the corresponding chromium complexes **2a-2d**, which were isolated as brown solids in good yields (62-91%) as presented in Scheme 1.



Scheme 1. Synthesis of chromium complexes 2a-2d.

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These complexes, which are air- and moisture-sensitive, show moderate solubility at room temperature in acetonitrile

and THF. The identity of **2a-2d** was established on the basis of elemental analysis, IR spectroscopy, and fight resolution thats spectrometry (HRMS) for **2a** and **2b**. All attempts to recrystallize the precatalysts **2a–2d** using various crystallization procedures failed resulting in amorphous materials, unfortunately not suitable for a single- crystal X-ray diffraction analysis. Thus, we decided to perform DFT calculations to estimate ground state optimized structures of chromium precatalysts **2a-2d** aiming to get more insight about their geometrical preferences.

Initially the DFT calculations were carried out in order to assess the relative stability of the *fac*- and *mer*-isomers of the Cr complexes. The relative free Gibbs energy values for the isomers are summarized in Table S1. In all cases, the *mer* isomers are more stable by 23.9-34.3 kcal mol<sup>-1</sup> than the *fac* isomers. Optimized *mer*-structures for the ground state obtained at the BP86/def2-TZVP level of theory are shown in Fig. 1. All complexes exhibited a slightly distorted octahedral geometries with *cis* bidentate S,N coordination of thioetherimine ligand, three chloride ligands, and the THF molecule completing the coordination sphere. DFT computed bond distances and bond angle values are listed in Table 1. The Cr-S [2.483-2.521 Å], Cr-N [2.069-2.126 Å], and Cr-Cl<sub>av</sub> [2.297-2.304 Å] bond distances are comparable in magnitude with related chromium structures reported in the literature.<sup>5b,6</sup>



Fig. 1 Ground state optimized structures of *mer*- $[Cr{N,S}(THF)CI_3]$  (2a-2d) at the BP86/def2-TZVP level of theory.

Table 1 Selected geometrical parameters for complexes 2a-2d.							
	2a	2b	2c	2d			
Cr-N	2.126	2.074	2.069	2.075			
Cr-S	2.483	2.480	2.480	2.521			
Cr-O	2.127	2.106	2.093	2.131			
Cr-Cl <sub>av</sub>	2.304	2.301	2.300	2.297			

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S-Cr-Cl	171.43	174.87	175.25	173.89
Cl-Cr-Cl	169.68	170.04	169.61	169.81

#### 2.2. Ethylene Oligomerization Results

Initial catalytic screening of 2a-2d was performed in toluene at 80 °C, 20 bar constant ethylene pressure, and using MAO containing 20 wt.% TMA as cocatalyst ([AI]/[Cr] = 300). The most relevant oligomerization results are listed in Table 2. The catalyst systems 2a-2d/MAO afforded a nonselective distribution of  $\alpha$ -olefins with moderate activity in ethylene oligomerization (TOF's = 3,400-26,600 mol(ethylene)·mol(Cr)-<sup>1</sup>·h<sup>-1</sup>) over 15-minute runs. Quite different results have been found for similar chromium complexes containing a pendant donor  $[Cr(MeS-2-PhCH=N-(CH_2)_2Y)Cl_3]$  (Y = PPh<sub>2</sub>; OMe, NMe<sub>2</sub>) where upon activation with MAO led to a primarily polymerization systems; in this case, the amounts of oligomers in the liquid fraction attained only 2.0-19.0 wt% of the total of products.<sup>7</sup> These contrasting results might be associate to the presence of third donor group to the thioether-imine backbone that hinders the formation of reduced chromium species, which is assumed to be responsible for the nonselective oligomerization behavior.4

As presented in Fig. 2, the substituents on the thioether and/or imine groups of the ligand play an important role on the catalytic performance of the precatalysts. In particular, the highest activity among the four precatalysts screened was reached with **2b** (TOF = 26,600 mol(ethylene)·mol(Cr)<sup>-1</sup>·h<sup>-1</sup>).

In order to investigate the steric effect of the thioetherimine ligands on the activity, the topographic steric maps of **2a-2d** were evaluated from the percent buried volume ( $%V_{bur}$ ) using the SambVca 2.1 software,<sup>8</sup> and metrical data from the optimized structures (Fig. 3). The results are compiled assuming a 3.50 Å for the sphere radius, omitted hydrogen atoms and scaled bond radii by 1.17, as recommended. The  $%V_{bur}$  values ranging from 42.1 to 44.5 imply that the substituents at thioether or imine group did not cause a significant influence on the steric properties of the chromium complexes. Thus, we can speculate that the catalytic activity is mainly controlled by electronic and not by steric effects of the substituent at the thioether/imine groups.

In general, the precatalysts bearing electron-donating substituents (*tert*-butyl, p-C<sub>6</sub>H<sub>4</sub>OMe) (**2a**, **2b** and **2d**) showed higher activities in comparison to **2c** containing an electron-withdrawing (i.e., phenyl) substituents. Furthermore, this positive effect on the catalytic performance is more pronounced for chromium complexes containing electron-donating substituents at the imine group (**2a** and **2b**). Hence, precatalyst **2a** with a *tert*-butyl group in the imine unit is ca. 2.7 times more active than **2d** that contains the same group bound to the thioether moiety (compare entries 1 and 4). Moreover, by comparing **2c** and **2d**, it was observed that the presence of phenyl group at the thioether unit led to a substantial decrease in the TOF. These results possibly arise from the poor coordination of the S-based ligands to Cr atom and thus destabilizing the Cr active species.<sup>5e-f</sup>



Fig. 2 Influence of the nature of chromium precatalyst 2a-2d on TOF and selectivity for oligomers (T = 80 °C, 20 bar, time = 15 min, [Al]/[Cr] = 300).



Fig. 3. Topographic steric maps of the thioether-imine ligands in 2a-2d.

All chromium complexes **2a-2d** produce oligomers ranging from C<sub>4</sub> to C<sub>14</sub><sup>+</sup> with a high selectivity for  $\alpha$ -olefins. As illustrated in Fig. 4, the selectivities within the liquid fraction are very similar indicating that the R<sup>1</sup> and R<sup>2</sup> have no significant influence on the product distribution. The distribution of oligomers obtained by the **2a-2d**/MAO systems follows Schulz–Flory rules with similar K values (K<sub>C4-C12</sub> $\approx$  0.90) as presented in Fig. 5.

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Page 4 of 10

#### Journal Name



reaction conditions such as [Al]/[Cr] molar ratio, cocatalyst type, run time and reaction temperatureoTbe1[A0]/[On] molar ratio was adjusted from 300 to 2000 (entries 1, 5-7, Table 2). When activated with 600 equiv. of MAO, precatalyst 2a led to slightly improved activity (TOF = 32,300 (mol ethylene) (mol Cr)<sup>-1</sup> h<sup>-1</sup>), with production of higher amount of lighter olefins  $[\alpha$ -C<sub>4</sub> (20.5 wt.%),  $\alpha$ -C<sub>6</sub> (19.9 wt.%) and  $\alpha$ -C<sub>8</sub> (18.0 wt.%)]. Varying the [Al]/[Cr] ratio from 600 to 1200 equiv. led to a significant enhancement in the activity (TOF = 207,500 (mol ethylene) (mol Cr)<sup>-1</sup> h<sup>-1</sup>) with similar oligomer distribution and high selectivity for  $\alpha$ -olefins (entry 6). Notably, the activation **2a** with 2000 equiv. led to a remarkable increase in the catalytic activity [TOF = 971,100 (mol ethylene) (mol Cr)<sup>-1</sup>  $h^{-1}$ ; 532,794 g/g of  $(r \cdot h^{-1})$ ], that is, 38-fold higher than that observed using 300 equiv. suggesting that excess cocatalyst was needed for complete activation. This activity compares well with other chromium complexes bearing thioether ligands,<sup>5</sup> Error! Bookmark not defined but definitively do not compete with PNP-Cr catalytic systems.<sup>9</sup> It is important to note that while the MAO loading affected substantially the activity, the selectivity for olefins remained almost unchanged (97.2-98.8 wt.%) (Fig. 6).

ig. 4 Sele -olefins (	ectivity (T = 80	a of <b>2a–2c</b> °C, 20 ba	<b>d</b> /MAO ol r, time = :	igomerizati	2d ion systen ]/[Cr] = 30	ns for 00)	with 20 activity g/g of 9 300 eq comple chromi defined.b system affecte remain	TTOF = 9 (TOF = 9) (ToF = 1)], th (uiv. sugge ete activa) um compl ut definit s. <sup>9</sup> It is im d substar ed almost	. led to a in 71,100 (minat is, 38-fine string that is, 38-fine string that iton. This leaves bear in the second string that the second string the second string the second string strin	remarka ol ethy old high activity ng thio not con o note activity ed (97.2	able increated by the increated by the increated by the increase of the increa	ease in the ol Cr) <sup>-1</sup> h <sup>-1</sup> that obse yst was r es well v nds, <sup>5</sup> Error th PNP-C e the MA lectivity %) (Fig. 6)	e catalytic <sup>1</sup> ; 532,794 rved using needed for with other ! Bookmark not cr catalytic AO loading for olefins
To opt recatalys <b>able 2</b> . Et	timize st <b>2a</b> w hylene	the catal as select Oligomer	yst in terr ed for fur rization wit	ms of activ ther screer th <b>2a-2d</b> pre	ity and sening unde ecatalyst sy	electivity, r various ystems. <sup>a</sup>							
						Olig	Oligomer Distribution (wt.%)						
Entry	Cat	T (min)	[Al/Cr]	TOF <sup>b</sup> (10 <sup>3</sup> ·h <sup>-1</sup> )	C <sub>4</sub> (α-C <sub>4</sub> )	C <sub>6</sub> (α-C <sub>6</sub> )	C <sub>8</sub> (α-C <sub>8</sub> )	C <sub>10</sub> (α-C <sub>10</sub> )	C <sub>12</sub> (α-C <sub>12</sub> )	C <sub>14+</sub>	Olig (wt.%)	PE (wt.%)	Total product (g)
1	2a	15	300	25.7	17.3 (94.4)	19.3 (95.5)	16.6 (95.1)	13.7 (89.2)	10.7 (80.1)	22.4	98.8	1.2	1.812
2	2b	15	300	26.6	16.7 (95.3)	19.5 (95.9)	17.3 (95.6)	14.3 (90.3)	11.2 (81.9)	21.0	95.5	4.5	1.947
3	2c	15	300	3.4	19.9 (90.1)	21.3 (91.2)	18.9 (87.1)	13.4 (87.5)	10.3 (70.5)	16.2	90.2	9.8	0.266
4	2d	15	300	9.6	19.0 (93.1)	20.8 (94.5)	18.3 (92.5)	14.3 (88.4)	10.8 (79.4)	16.8	97.2	2.8	0.689
5	2a	15	600	32.3	21.9 (93.5)	20.9 (95.1)	19.2 (93.9)	14.7 (94.5)	11.0 (93.3)	12.3	97.2	2.8	2.324
6	2a	15	1200	207.5	17.2 (96.0)	19.7 (96.3)	17.9 (96.4)	14.7 (96.4)	12.6 (96.3)	17.9	98.2	1.8	14.770
7	2a	15	2000	971.1	15.7 (93.8)	18.9 (94.9)	17.9 (94.8)	15.4 (94.5)	12.8 (94.4)	19.3	98.0	2.0	69.253
8 <sup>d</sup>	2a	15	900	14.9	19.8 (84.2)	20.8 (84.9)	17.8 (80.5)	14.9 (80.5)	10.8 (78.9)	15.9	97.3	2.7	1.069
9 <sup>e</sup>	2a	15	900	26.0	35.5 (81.3)	11.7 (100)	13.6 (57.7)	16.0 (29.0)	10.2 (25.8)	13.0	87.5	12.5	2.079
10	2a	5	300	28.1	18.5 (90.6)	20.7 (92.5)	18.2 (93.0)	13.9 (92.0)	10.2 (84.4)	18.5	98.3	1.7	0.722
11	2a	30	300	10.9	16.1 (95.4)	19.7 (95.6)	18.2 (94.4)	14.4 (95.5)	11.3 (95.3)	20.3	92.3	7.7	1.656
12 <sup><i>f</i></sup>	<b>2</b> a	15	300	1.1	31.4 (79.7)	28.0 (81.8)	18.0	10.3 (100)	6.7 (100)	5.6	31.9	68.1	0.251
13 <sup>g</sup>	<b>2</b> a	15	300	11.0	14.6 (94.3)	18.3	17.3 (91.6)	14.0	11.4	24.4	94.7	5.3	0.813

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<sup>a</sup> Reaction conditions unless specified otherwise: toluene = 40 mL, [Cr] = 10 µmol, oligomerization time = 15 min, P(ethylene) = 20 bar (kept constant), T = 80 °C, MAO. The results shown are representative of at least duplicated experiments, yielding reproducible results within ±5%. <sup>b</sup> Mol of ethylene converted (mol of Cr)<sup>-1</sup>·h<sup>-1</sup> as determined by quantitative GLC. <sup>c</sup>C<sub>n</sub>, percentage of olefin with n carbon atoms in oligomers;  $\alpha$ -C<sub>n</sub>, percentage of terminal alkene in the C<sub>n</sub> fraction, as determined by quantitative GLC.<sup>d</sup> [TMA] = 600, [MAO] = 300.<sup>e</sup> [TIBA] = 600, [MAO] = 300; <sup>f</sup> T = 60 °C;<sup>g</sup> T = 100 °C.

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**Fig. 5** Oligomers distribution produced by **2a-2d**/MAO oligomerization systems ( $C_4$ - $C_{12}$ ) (80°C, 20 bar, [Al/[Cr] = 300). (a) Schulz–Flory  $\alpha$ -olefin distribution in molar percentage and (b) plot of the log(mol%) of vs carbon number.

The activation of 2a with pure trimethylaluminum (TMA) or triisobutylaluminum (TIBA) afforded only a small amount of polymer. Thus, an exploratory study was performed by addition of external alkyl aluminum (TMA or TIBA) together with MAO aiming at verifying the influence of these reducing agents on the catalytic performance of 2a. The addition of 600 equiv. of TMA to the 2a/MAO(300) catalyst system decreases the activity (TOF = 14,900 (mol ethylene) (mol Cr)<sup>-1</sup> h<sup>-1</sup>) with production of enriched fractions in  $C_4$ - $C_{10}$  (73.3 wt.%) and concomitant decrease in  $C_{14}^+$  (15.9 wt.%)(compare entries 1 and 8). On the other hand, the activation of 2a with MAO (300 equiv.)/TIBA (600 equiv.) resulted in similar activity but with a substantial increase in 1-butene [from 16.3 to 28.9 wt.%]. Furthermore, the presence of TIBA in the oligomerization medium causes a dramatic loss in selectivity toward formation of  $\alpha$ -olefins in the range of  $C_6$ - $C_{12}$  along with production of higher amount of polymer (12.5 wt.%). The results above mentioned suggest that the use of these alkyl aluminums in combination with MAO might be influencing the nature of the catalytically active species.<sup>10</sup>



Fig. 6 Influence of [AI]/[Cr] molar ratio on TOF and selectivity using **2a**/MAO oligomerization system (80°C, 20 bar, 15 min).

The selectivities, product distribution and productivity were monitored versus time (5, 15 and 30 min) with [Al]/[Cr] molar ratio of 300 and the temperature at 80 °C for investigating the lifetime of the active species. (entries 1, 10 and 11). As can be seen in Fig. 7, the total mass of products increased significantly from 5 to 15 min.



**Fig.7** Monitoring of selectivities and productivities as a function of time in the ethylene oligomerization reaction promoted by the **2a**/MAO system (T = 80 °C, 20 bar of ethylene, [AI]/[Cr] = 300).

On prolonging the reaction time (30 min), it was not observed a significant variation in total mass of products (oligomers and polymer), which are comparable considering an average error of  $\pm$  5%, indicating that **2a** had a minimal catalytic lifetime of 15 min. It should be pointed out that the higher

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#### ARTICLE

amount of polymer obtained in 30 min (7.7 wt.%) suggest that the nature of the active species varied over time. However, no significant variation in the selectivities for  $\alpha$ -olefins (C<sub>4</sub>-C<sub>12</sub>) was observed over a 5-30 min period (92.6-94.8 wt.%), indicating that parallel chain isomerization processes are a minor pathway in these oligomerization reactions.

The optimal operating temperature for this class of precatalysts is 80 °C. At 60°C the oligomerization activity of the **2a**/MAO dropped significantly, and a large amount of polymer was produced (68.1 wt.%). On elevating the oligomerization temperature from 80°C to 100°C, the precatalyst still operating but with lower activity (11,000 mol(ethylene)·mol(Cr)<sup>-1</sup>·h<sup>-1</sup>), which can be associated to the partial deactivation of the active species and the lower solubility of ethylene in toluene at 100 °C. However, the selectivity for  $\alpha$ -olefins remains almost unchanged, and only 5.3 wt.% of the product formed was PE (compare entries 1 and 13).

The DSC curves of polymers produced by **2a** showed that the melting temperature (T<sub>m</sub>) is depend of the reactional conditions. Thus, the use of TIBA/TMA or combination of these ones with MAO generated polymers with a single melting transition in the range of 125.2-133.8 °C (Fig. S7) On the other hand, the polymers produced at higher temperature (100 °C) or using higher MAO loading (1200 equiv.) displayed two major endothermic peaks at in the range of 69–127.1 °C suggesting the production of linear oligoethylenes with low molecular weight (Fig. S8). Similar results were observed with other catalytic systems based on chromium complexes bearing bi- and tridentate ligands.<sup>11</sup>

# 3. Conclusions

We have described the synthesis of a new class of chromium complexes bearing thioether-imine bidentate ligands. Based on the relative free Gibbs energy values, the most energetically preferred structure was the mer configuration. All precatalysts, upon activation with MAO, generated active species affording a nonselective distribution of  $\alpha$ -olefins along with the production of varied amounts of polymers. The  $\alpha$ -C<sub>4</sub> is the largest component in the liquid fraction suggesting that this class of precatalysts operates via a Cossee-Arlman mechanism. Considering the similar  $%V_{bur}$  values for 2a-2d, we speculate that catalytic activity is mainly controlled by electronic effects of the substituent at the thioether/imine groups. Thus, the precatalysts bearing electron-donating substituents (tert-butyl, p-C<sub>6</sub>H<sub>4</sub>OMe) (2a, 2b and 2d) showed higher activities in comparison to 2c containing an electron-withdrawing (i.e., phenyl) substituent. Furthermore, this positive effect on the catalytic performance is more pronounced for chromium complexes containing electron-donating substituents at the imine group (2a and 2b). The optimization study showed that this class of catalysts displayed better activities at high MAO loading ([Al]/[Cr] = 2000) and oligomerization polymerization temperature of 80°C. Furthermore, this class of ligands is not able to guarantee a long lifetime, as the catalyst undergoes almost complete deactivation after 15 min. The use of a mixture of cocatalysts such as TIBA/MAO causes a dramatic loss in

selectivity toward formation of  $\alpha$ -olefins in the range of the selectivity toward formation of a contract of the selection of higher amount of the selection of higher amount of the selection of the selection

## 4. Experimental

#### 4.1. General Procedures

All manipulations involving air- and/or moisture-sensitive compounds were carried out in an MBraun glovebox or under dry argon using standard Schlenk techniques. Toluene, THF, and hexane were dried over a Braun MB-SPS-800 solvent purification system. Other solvents were dried from the appropriate drying agents under argon before use. CrCl<sub>3</sub>(THF)<sub>3</sub> was purchased from Sigma-Aldrich and used as received. Ethylene (White Martins Co.) and argon were deoxygenated and dried through BTS columns (BASF) and 3Å activated molecular sieves prior to use. MAO (Witco, 5.21 wt.% Al solution in toluene, 20 % TMA), triisobutylaluminum (TIBA) (Sigma-Aldrich, 1M in hexane) and trimethylaluminum (TMA) (Sigma-Aldrich, 2M in toluene) were used as received. Infrared spectra were performed on neat products using a FT-IR Bruker Alpha Spectrometer operating in the ATR mode. NMR spectra of the ligands were recorded on a Varian MR-400 spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are reported in ppm vs. SiMe<sub>4</sub> and were determined by reference to the residual solvent peaks. Elemental analyses were performed by the Analytical Central Service of the Institute of Chemistry-UFRGS (Brazil) and are the average of two independent determinations. High-resolution mass spectrometry (HRMS) data were collected on a Micromass Waters<sup>®</sup> Q-Tof spectrometer. Quantitative gas chromatographic analysis of ethylene oligomerization products was performed on a Agilent 7890A instrument equipped with a Petrocol HD capillary column (methyl silicone, 100 m length, 0.25 mm i.d. and film thickness of 0.5  $\mu m)$  (36 °C for 15 min, then heating at 5 °C·min<sup>-1</sup> until 250 °C); cyclohexane was used as internal standard. Polymer melting points were measured by differential scanning calorimetry (DSC) with a TA DSC Q20 using a heating rate of 10 °C min<sup>-1</sup> after twice previous heating to 180 °C and cooling to 40 °C at 10 °C min<sup>-1</sup>.

#### 4.2. Synthesis of thioether-imine ligands

4.2.1. PhS-2-PhCH=N-<sup>t</sup>Bu (1a). To a stirred solution containing 2-(phenylthio)benzaldehyde (0.32 g, 1.49 mmol) in dried methanol (3 mL), tert-butylamine (0.11g, 1.49 mmol) was added. The reaction mixture was stirred for 3 h at 25 °C. Evaporation of methanol gave a brown oil residue, which was purified using a Kugerloh distillation apparatus under reduced pressure (130 °C at 2 mmHg). 1a was obtained as brown oil (0.33 g, 76%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): 8.94 (1H, s), 8.33 (1H, d, <sup>3</sup>J<sub>HH</sub>=7.81 Hz), 7.34 (1H, d, <sup>3</sup>J<sub>HH</sub>=7.51 Hz), 7.15-6.83 (7H, m), 1.16 (9H, s). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C): 29.32, 57.50, 126.07, 128.14, 128.21, 129.02, 129.12, 130.29. 133.92, 135.01, 137.29, 138.09, 153.09. IR (ATR, cm-1): n 376 (w), 442 (m), 470 (m), 511 (w), 614 (w), 687 (s), 737 (s), 856 (w), 909 (w), 966 (w), 1022 (m), 1057 (w), 1073 (w), 1198 (s), 1217 (m), 1271 (m), 1371 (m), 1440 (s), 1459 (s), 1477 (s), 1581 (m), 1628 (m), 1694 (w), 1725 (w), 2859 (w), 2925 (w), 2965 (m), 3057 (w). HRMS (ESI,

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MeOH, positive ions) m/z calcd. for  $C_{17}H_{20}NS$  [**1a**-H]<sup>+</sup>: 270.1316, found 270.1318.

4.2.2. PhS-2-PhCH=NC<sub>6</sub>H<sub>4</sub>-4-OMe (1b) Pro-ligand 1b was prepared using a modification of the literature method.<sup>12</sup> This product was prepared as described above for 1a, starting from 2-(phenylthio)benzaldehyde (0.29 g, 1.37 mmol) and pmethoxyaniline (0.17 g, 1.37 mmol). 1b was obtained as a dark brown oil (0.32 g, 73%). <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>, 25 °C): 9.05 (1H, s), 8.23 (1H, m), 7.48-7.29 (8H, m), 7.15 (2H, d, <sup>3</sup>*J*<sub>HH</sub>=8.84 Hz), 6.94 (2H, d, <sup>3</sup>*J*<sub>HH</sub>=8.85 Hz), 3.61 (3H, s). <sup>13</sup>C NMR (100 MHz, acetone-d<sub>6</sub>, 25 °C): 54.84, 126.99, 128.33, 129.50, 129.84, 131.39, 133.80, 135.97, 136.33, 136.89, 144.65, 155.64, 158.73. IR (ATR, cm<sup>-1</sup>): v 384 (w), 399 (w), 432 (w), 456 (w), 525 (w), 540 (m), 620 (w), 688 (m), 720 (w), 750 (s), 760 (s), 804 (m), 825 (m), 880 (w), 970 (w), 1031 (w), 1053 (w), 1104 (w), 1158 (w), 1190 (w), 1241 (s), 1263 (w), 1299 (w), 1353 (w), 1429 (m), 1461 (m), 1505 (s), 1591 (w), 1610 (m), 2831 (w), 2901 (w), 2925 (w), 2954 (w), 2997 (w), 3064 (w). HRMS (ESI, MeOH, positive ions) *m/z* calcd. for C<sub>20</sub>H<sub>18</sub>NOS[**1b**-H]<sup>+</sup>: 320.1109, found 320.1112.

**4.2.3.** PhS-2-PhCH=N-C<sub>6</sub>H<sub>5</sub> (1c) Pro-ligand 1c was prepared using a modification of the literature method.<sup>12</sup> This product was prepared as described above for 1a, starting from 2-(phenylthio)benzaldehyde (0.27 g, 1.25 mmol) and aniline (0.12 g, 1.25 mmol). 1c was obtained as a brown oil (0.26 g, 72%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): 9.17 (1H, s), 8.43 (1H, d, <sup>3</sup>*J*<sub>HH</sub>=7.74 Hz), 7.28 (1H, d, <sup>3</sup>*J*<sub>HH</sub>=7.77 Hz), 7.16-6.85 (12 H, m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C): 121.40, 126.27, 126.83, 128.36, 129.09, 129.38, 129.56, 130.02, 134.15, 136.90, 137.04, 137.38, 152.63, 158.23. IR (ATR, cm<sup>-1</sup>): n 428 (w), 456 (f), 507 (w), 543 (m), 685 (s), 738 (s), 760 (s), 825 (w), 908 (w), 970 (w), 1021 (w), 1063 (w), 1118 (w), 1161 (w), 1190 (m), 1266 (w), 1354 (w), 1463 (m), 1483 (s), 1580 (s), 1617 (m), 1693 (m), 2907 (w), 3019 (w), 3052 (w). HRMS (ESI, MeOH, positive ions) *m/z* calcd. for C<sub>19</sub>H<sub>16</sub>NS [1c-H]<sup>+</sup>: 290.1003, found 290.1006.

**4.2.4.** <sup>t</sup>BuS-2-PhCH=N-C<sub>6</sub>H<sub>5</sub> (1d) This product was prepared as described for 1a, starting from above (tertbutylthio)benzaldehyde (0.29 g, 1.50 mmol) and aniline (0.14 g, 1.50 mmol). 1d was obtained as a yellow oil (0.29 g, 71%). 1H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): 9.57 (1H, s), 8.62 (1H, dd, <sup>3</sup>J<sub>HH</sub>=1.67, 7.85 Hz), 7.52 (1H, dd, <sup>3</sup>J<sub>HH</sub>=1.37, 7.72 Hz), 7.35-7.33 (2H, m), 7.21-7.03 (5H, m), 1.08 (9H, s). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C): 30.59, 46.84, 121.10, 125.85, 127.99, 129.12, 129.28, 130.37, 134.76, 139.57, 140.88, 152.66, 159.95. IR (ATR, cm<sup>-1</sup>): n 435 (w), 500 (w), 540 (w), 692 (s), 750 (s), 801 (w), 869 (w), 905 (w), 970 (w), 1024 (s), 1096 (w), 1154 (w), 1186 (w), 1262 (w), 1357 (w), 1436 (w), 1461 (w), 1483 (w), 1580 (w), 1621 (w), 1649 (w), 1692 (w), 2852 (w), 2917 (w), 2964 (w), 3055 (w). HRMS (ESI, MeOH, positive ions) m/z calcd. for C<sub>17</sub>H<sub>20</sub>NS [1d-H]\*: 270.1316, found 270.1327.

#### 4.3. Synthesis of Chromium (III) Complexes

4.3.1. [Cr(PhS-2-PhCH=N-<sup>t</sup>Bu)(THF)Cl<sub>3</sub>] (2a) A solution of 1a (0.20
g, 0.74 mmol) in THF (10 mL) was added dropwise over a period of 10 minutes to a solution of [CrCl<sub>3</sub>(THF)<sub>3</sub>] (0.27 g, 0.74 mmol) in THF (15mL) at room temperature under constant stirring. The resulting solution was allowed to stir for 3 h at room 60

temperature, and then the solvent was removed under vacuum. The solid residue was washed repeatedly with CORCTHE (35%22 mL) and diethyl ether (3 x 10 mL) to give, after drying, **2a** as a brown solid (0.33 g, 91%). IR (ATR, cm<sup>-1</sup>): v 512 (w), 576 (w), 689 (s), 757 (s), 850 (s), 919 (w), 1009 (m), 1041 (m), 1082 (w), 1095 (w), 1173 (w), 1227 (m), 1241 (m), 1277 (w), 1302 (w), 1338 (w), 1425 (w), 1447 (w), 1465 (w), 1493 (m), 1518 (w), 1547 (w), 1583 (w), 1597 (w), 2875 (w), 2971 (w). Anal. Calcd. for C<sub>21</sub>H<sub>27</sub>Cl<sub>3</sub>CrNOS: C: 50.46, H: 5.44, N: 2.80. Found: C: 49.92, H: 5.13, N: 2.47. HRMS (ESI, MeOH, positive ions) m/z calcd. for C<sub>21</sub>H<sub>27</sub>Cl<sub>3</sub>CrNOS [M-Cl]<sup>+</sup>: 463.0596, found 463.0591.

**4.3.2.** [Cr(PhS-2-PhCH=N-C<sub>6</sub>H<sub>4</sub>-4-OMe)(THF)Cl<sub>3</sub>] (2b) This complex was prepared as described above for 2a, starting from 1b (0.31 g, 0.97 mmol) and [CrCl<sub>3</sub>(THF)<sub>3</sub>] (0.36 g, 0.97 mmol) in THF (15 mL) to give 2b as a brown solid (0.32 g, 62%). IR (ATR, cm<sup>-1</sup>): v 458 (w), 503 (m), 670 (w), 689 (m), 747 (m), 824 (m), 862 (w), 916 (w), 1020 (m), 1117 (w), 1126 (w), 1171 (m), 1197 (w), 1257 (s), 1303 (w), 1405 (w), 1438 (w), 1456 (w), 1473 (w), 1506 (s), 1558 (sh), 1579 (m), 1601 (w), 1643 (w), 1674 (w), 1690 (w), 2932 (w), 2963 (w), 3045 (w). Anal. Calcd. for C<sub>24</sub>H<sub>25</sub>Cl<sub>3</sub>CrNO<sub>2</sub>S: C: 52.42, H: 4.58, N: 2.55. Found: C: 52.04, H: 4.16, N: 2.24. HRMS (ESI, MeOH, positive ions) m/z calcd. for C<sub>20</sub>H<sub>19</sub>Cl<sub>3</sub>CrNO2S [M+H<sub>2</sub>O-THF-Cl]<sup>+</sup>: 458.9919, found 458.9914.

**4.3.3.** [Cr(PhS-2-PhCH=N-C<sub>6</sub>H<sub>5</sub>)(THF)Cl<sub>3</sub>] (2c) This complex was prepared as described above for 2a, starting from 1c (0.23 g, 0.79 mmol) and [CrCl<sub>3</sub>(THF)<sub>3</sub>] (0.29 g, 0.79 mmol) in THF (15 mL) to give 2c as a brown solid (0.30 g, 74%). IR (ATR, cm<sup>-1</sup>): v 444 (w), 505 (w), 525 (w), 5771 (w), 614 (w), 691 (s), 752 (s), 803 (w), 874 (w), 997 (w), 1023 (s), 1046 (s), 1112 (sh), 1152 (w), 1176 (w), 1227 (w), 1261 (w), 1437 (m), 1469 (m), 1493 (s), 1554 (m), 1578 (m), 1600 (s), 1627 (sh), 2871 (w). Anal. Calcd. for  $C_{23}H_{23}Cl_3CrNOS$ : C: 53.14, H: 4.46, N: 2.69. Found: C: 52.78, H: 4.07, N: 2.33.

**4.3.4.** [Cr(<sup>†</sup>BuS-2-PhCH=N-C<sub>6</sub>H<sub>5</sub>)(THF)Cl<sub>3</sub>] (2d) This complex was prepared as described above for 2a, starting from 1d (0.19 g, 0.70 mmol) and [CrCl<sub>3</sub>(THF)<sub>3</sub>] (0.26 g, 0.70 mmol) in THF (15 mL) to give 2d as a brown solid (0.29 g, 84%). IR (ATR, cm<sup>-1</sup>): v 470 (w), 481 (w), 499 (w), 540 (w), 575 (w), 616 (w), 638 (w), 687 (w), 757 (m), 926 (s), 985 (m), 1028 (w), 1160 (w), 1188 (w), 1261 (w), 1295 (w), 1318 (w), 1361 (w), 1400 (sh), 1429 (w), 1455 (w), 1472 (w), 1493 (w), 1577 (w), 1600 (w), 1619 (w), 1646 (w), 1693 (w), 2917 (w), 2959 (w), 3007 (w). Anal. Calcd. for C<sub>21</sub>H<sub>27</sub>Cl<sub>3</sub>CrNOS: C: 50.46, H: 5.44, N: 2.80. Found: C: 50.08, H: 5.32, N: 2.67.

# 4.4 General oligomerization procedure

Ethylene oligomerization reactions were performed in a 100 mL double-walled stainless Parr reactor equipped with mechanical stirring, internal temperature control and continuous feed of ethylene. The Parr reactor was dried in an oven at 120 °C for 5 h prior to each run, and then cooled under vacuum for 30 min. A typical reaction was performed by introducing toluene (30 mL) and the proper amount of cocatalyst into the reactor under an ethylene atmosphere. After 20 min, the toluene catalyst solution (10 mL, [Cr] = 10  $\mu$ mol) was injected into the reactor

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58 59 60 under a stream of ethylene and then the reactor was immediately pressurized. Ethylene was continuously fed in order to maintain the desired ethylene pressure. After 20 min, the reaction was stopped by cooling the system to -60 °C and depressurizing. An exact amount of cyclohexane was introduced (as an internal standard) and the mixture was analyzed by quantitative GLC. The polymer was separated by filtration, washed with small portions of acidic ethanol, then ethanol and water, and the resulting material was dried in a vacuum oven at 60 °C for 12 h.

# 4.5 Computational methods

All simulations were performed using the ORCA 4.0.1.2 package<sup>13</sup> with the BP86 functional<sup>14</sup> and Ahlrichs' def2-TZVP basis set<sup>15</sup> with the def2/J auxiliary basis set.<sup>16</sup> Resolution of identity approximation<sup>17</sup> and Grimme's dispersion correction<sup>18</sup> were used throughout all calculations. All optimized structures are confirmed as stationary points as no imaginary frequencies were found.

# **Conflicts of interest**

There are no conflicts to declare.

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Chromium complexes bearing thioether-imine ligands were synthesized and their catalytic behavior in ethylemed Article Online oligomerization has been investigated evaluating the role of the ligand, and the experimental parameters on the activity, selectivity, and product distribution.

